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(54) Title: PROCESS FOR TREATING LATEX-CONTAINING WASTE WATER

(57) Abstract

A process for treating latex-containing waste water to produce reusable latex and water, the quality of the water being sufficiently high for reuse or discharge to a water course. The waste water (2) is delivered directly to a reverse osmosis membrane unit (6) without any pre-treatment, and pressure is applied across the membrane to separate the waste water into permeate (7) and retentate. The membrane may be a tubular structure defining channels through which the waste water is pumped, those channels having a flow cross section sufficient to enable flow rates to be maintained that prevent blockage.

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PROCESS FOR TREATING LATEX-CONTAINING WASTE WATER

The present invention relates to a process for removing latex from latex-containing waste water.

Latex-containing waste waters are produced during the manufacture and use of latex products such as binders for paints and the like. Such waste waters include latex and dissolved organic substances such as surfactants which are present in order to maintain the stability of the latex.

Various approaches have been adopted to the treatment of latex-containing waste waters. For example it is well known to treat such waste waters by flocculation to remove suspended solids for landfill disposal. The resultant supernatant which contains the bulk of the water and a high level of dissolved organic substances including surfactants is then either sent to a waste water treatment plant for further processing or discharged to a waterway in the hope that natural processes will further degrade the organic substances. Over time, however, regulations have made it progressively more difficult to discharge the supernatant to waterways, and the costs of landfill and further supernatant treatment have increased dramatically.

Considerable research effort has been directed towards using ultrafiltration processes for the treatment of latex-containing waste waters. As indicated by European Patent 0512736 and U.S. Patent No. 4160726, however, ultrafiltration has a major drawback in that the surfactants and other small molecules which stabilise the latex are not retained with the latex but rather remain in the water. The latex retentate is accordingly of little commercial value and the permeate water is contaminated by the organic substances which are not retained with the latex. Accordingly it is still not possible to discharge the permeate water without further expensive treatments, for example activated carbon adsorption or reverse osmosis.

Reverse osmosis (referred to by the letters RO below) has been widely used for the production of potable and pure water from sea water or other water sources. It has also been used for cleaning waste water from pulp mills and dyehouses, and for concentrating for example fruit juices. Various RO membrane modules are commercially available, for example hollow fibre and spiral wound modules which

are used in circumstances in which the fluid to be treated does not contain large amounts of particulate material, and tubular or plate and frame modules which define relatively larger channels through which the fluid to be treated is pumped and accordingly are less likely to become clogged.

It is evident from a review of literature on RO applications that there is a belief that membrane fouling is a determining factor for the success of RO processes. It has been supposed that colloids are a major contributor to the fouling of RO membranes and therefore must be removed by pre-treatment. Generally cartridge filtration or ultrafiltration are the methods used for pre-treating material to be processed by RO. Even in the case of relatively simple applications such as the desalination of seawater pre-treatment has been seen as playing a vital role in fouling control.

In the case of latex-containing waste waters, it has been proposed to initially treat the waste water using ultrafiltration, resulting in a permeate which is free from colloidal and other potential fouling materials, and to then further treat the permeate to remove surfactants and other low molecular weight compounds by RO. Presumably this approach was adopted in the past because latex is itself a colloidal material and could therefore be expected to cause very rapid fouling of RO membranes.

Latex-containing waste water is notoriously difficult to pump, firstly because high shear pumps tend to damage the latex, reducing its commercial value, and secondly because the latex itself tends to solidify on pump seals, resulting in heavy wear and rapid mechanical failure. These problems have proved difficult to overcome in ultrafiltration units which generally operate at pressures below 10 barg. As is well known RO processes generally require much higher pressures, for example above 35 barg, and might therefore be expected to be impractical in the treatment of latex-containing waste water without pre-treatment.

It is an object of the present invention to obviate or mitigate the problems outlined above.

According to the present invention, there is provided a process for removing latex from waste water, wherein the waste water is delivered directly to a reverse osmosis membrane unit, and pressure

is applied across a membrane defined by the membrane unit to drive water through the membrane, the membrane unit defining channels through which the waste water is pumped which channels have flow cross-sections sufficient to enable flow rates to be maintained that prevent channel blockage.

It has surprisingly been discovered that by appropriate system design reverse osmosis membranes can be used for the removal of latex from waste water without the membranes becoming clogged. Preferably the membranes comprise tubular membranes having a diameter of from 10 to 25 mm but alternative membrane types having the required flow characteristics can be used, for example plate and frame reverse osmosis membranes.

It has been found to be advantageous to use a high speed diaphragm pump operating at 1,000 strokes per minute or more. In contrast to low speed diaphragm pumps which operate typically at less than 100 strokes per minute and have a consequent tendency to generate low frequency pressure pulses, high speed diaphragm pumps tend to average out the pressure applied to the membranes.

The process in accordance with the present invention can be operated in a batch system or a continuous system. In a batch system, a batch of waste water is delivered from a feed source to a batch tank and the waste water is pumped through the membrane channels from the batch tank. The retentate from the membrane is recirculated to the batch tank, whereas the permeate is initially delivered to a permeate outlet, for example a clean water outlet tank. Once the batch process has been operating for some time, however, the concentration in the permeate of unwanted components such as surfactants increases to such a level that the permeate cannot be delivered to the clean water tank. Accordingly, once such a level of concentration is reached the permeate is re-circulated to the feed source. At the end of the batch process, the retentate is discharged to a retentate outlet, for example an outlet tank.

In the batch process, a high speed diaphragm pump operating at for example greater than 1,500 strokes per minute can be used to deliver waste water to the membrane unit at a pressure of greater than 35 bar g.

The permeate may be recycled to the waste water source once

the surfactant content reaches a level of, for example, two parts per million.

In the continuous process, waste water is delivered from a feed source to a first reverse osmosis membrane unit, the retentate of which is delivered to a second membrane unit or a series of further membrane units. The permeate from the first membrane unit is delivered to a permeate outlet, whereas the permeate from the second or each of the further membrane units is recirculated to the waste water source. Preferably there are three membrane units each fed by a high speed diaphragm pump. The speed of the diaphragm pumps decreases from the first membrane unit to the last, whereas the pressure delivered by the diaphragm pumps increases from the first membrane unit to the last. For example in the three membrane unit system the speed can decrease from greater than 2,000 strokes, to greater than 1,500 strokes, to greater than 1,000 strokes, whereas the pressure can increase from greater than 35 barg, to greater than 40 barg, to greater than 45 barg.

Embodiments of the present invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Fig. 1 illustrates the batch operation of the present invention; and

Fig. 2 illustrates the continuous operation of the present invention.

Referring to Fig. 1, the illustrated equipment is suitable for treating, for example, 60,000 litres per day (lpd) of a white water containing 0.5% latex solids and 46 ppm surfactants. A feed holding tank 1 has a capacity of 60,000 litres and receives waste water indicated by the arrow 2. A feed transfer pump 3 delivers waste water to a batch tank 4 having a capacity of 1,250 litres. Two high speed diaphragm pumps represented by a single pump 5 each deliver 90 litres per minute of the content of the batch tank 4 to a tubular reverse osmosis membrane unit 6. Each of the pumps 5 operates at 1,800 strokes per minute and at a pressure of 50 barg.

The membrane unit 6 incorporates reverse osmosis tubular membranes having an internal diameter of 12.3 mm. These provide a total surface area of 97.2 square metres. The retentate from the

membrane unit 6 is simply re-circulated to the batch tank 4. The permeate is delivered to a line 7 and initially flows through a valve 8 to a clean water tank 9 from which the water can be discharged or re-used. As the process continues, however, the concentration of surfactant in the permeate increases and once this concentration has reached a certain predetermined limit the valve 8 is closed and a valve 10 is opened to re-circulate the permeate of high chemical oxygen demand to the feed holding tank 1. At the end of the process the solids content in the batch tank 4 is discharged through the valve 7 to a product tank 11 from whence it can be recycled to the manufacturing process which resulted in the initial generation of the waste water.

Typically in operation the batch tank 4 will be filled with 1,250 litres of white water from the feed holding tank by the pump 3. The latex in the white water is concentrated by the membrane unit to 40% solids and is then discharged into the product tank 11. 1,000 litres of permeate with an average surfactant concentration of 2 ppm is collected into the clean water tank 9 and 235 litres of permeate containing on average 5 ppm surfactant is returned to the feed holding tank 1. The batch operation typically takes 25 minutes to complete and up to fifty such operations can be carried out in a 24 hour period.

It will be appreciated that the process described with reference to Fig. 1 has only two outputs, that is the re-usable latex delivered to the product tank 11 and the re-usable or dischargeable water delivered to tank 9. There is no requirement for further processing or for land fill site disposal.

A membrane system having the general structure of the system shown in Fig. 1 was used to process two white water samples. The system used comprised a feed holding tank 1 of 200 litres capacity, a high speed diaphragm pump 5 operating at 2700 strokes per minute and delivering 20 litres per minute at 40 barg and a tubular RO unit 6 with 12.3 mm diameter tubes and a membrane area of 1.8 m². The membrane was of a polyamide type with a characteristic rejection of 80% for NaCl.

The first sample white water feed was a blend of 5 different latex products of the acrylic type. Such products are commonly used

as tackifiers in glues or inks. The white water feed had the following composition:

Feed volume	2000 litres
Total solid content, w/v	0.5%
Total soluble Chemical Oxygen Demand, COD	350 mg/l
Zinc, as a soluble complex	60 ppm
Total surfactants	50 ppm

The COD was due mainly to surfactants, monomers, organic peroxides, and by-products. The surfactants were a mixture of ionic and non-ionic surfactants with not less than 25 different types.

The feed was concentrated to a total solid content of 5% in ten separate batches. The combined concentrate was then further concentrated to give the overall results below:

Volume of concentrate	25 litres
Total solid content, w/v	40%
Total soluble Chemical Oxygen Demand, COD	11410 mg/l
Zinc, as a soluble complex	4788 ppm
Total surfactants	3684 ppm

The permeate from the ten initial batches and the permeate from the final concentration step was combined to give the overall results below:

Volume of permeate	1975 litres
Total solid content, w/v	0%
Total soluble Chemical Oxygen Demand, COD	210 mg/l
Zinc, as a soluble complex	0.15 ppm
Total surfactants	4 ppm

The second sample white water feed was processed in a system that differed from that used to process the first sample only in that the membrane was of a polyamide type with a characteristic rejection of 99% for NaCl.

The second sample white water feed was a mixture of latex

7.

products of several types including acrylic, polyvinyl acetate and polystyrene types. Such products are commonly used as bonding agents, sealers, or binders in adhesives, roof coatings and floor screeds. The feed had the following composition:

Feed volume	200 litres
Total solid content w/v	2.3%
Total soluble Chemical Oxygen Demand, COD	480 mg/l

The COD was due mainly to surfactants, monomers, organic peroxides and by-products.

The feed was concentrated in a single batch to give the following results:

Volume of concentrate	9.58 litres
Total solid content, w/v	48%
Total soluble Chemical Oxygen Demand, COD	6204 mg/l
Volume of permeate	190.42 litres
Total solid content, w/v	0%
Total soluble Chemical Oxygen Demand, COD	192 mg/l

Referring now to Fig. 2, this illustrates a continuous process for treating 60,000 LPD of a white water containing 0.5% latex solids and 46 ppm surfactants. The system comprises a feed holding tank 12 of 60,000 litres capacity, a feed transfer pump 13, three reverse osmosis tubular membrane stages 14, 15 and 16, a latex outlet tank 17, a permeate outlet tank 18, and associated pumps and pipework. A high speed diaphragm pump 19 operates at 2,700 strokes per minute delivering 140 litres per minute at 40 barg. A high speed diaphragm pump 20 operating at 1,900 strokes per minute delivers 100 litres per minute at 45 barg. A high speed diaphragm pump 21 operating at 1,000 strokes per minute delivers 40 litres per minute at 50 barg. The membrane unit 14 comprises 12.3 millimetre internal diameter reverse osmosis membrane tubes with a total surface area of 75.6 square metres. The membrane unit 15 comprises reverse osmosis membrane tubes having internal diameters of 12.3 millimetres with a total surface

area of 40.5 square metres. The membrane unit 16 comprises reverse osmosis membrane tubes having an internal diameter of 12.3 millimetres and a total surface area of 10.82 square metres. Each of the tubular membranes comprises an active layer cast on a permeable tube which is further supported on a perforated stainless steel tube.

In operation of the system illustrated in Fig. 2, white water is drawn from the feed holding tank 12 by the pump 13 and supplied to the first membrane stage 14 at a typical rate of 2,500 litres per hour. The first membrane unit 14 removes water at a rate of 2469 litres per hour, the water leaving the first membrane unit 14 containing approximately 2 ppm surfactants. The partially concentrated retentate from the first membrane unit is drawn into the second membrane unit 15 by pump 20 where the latex is further concentrated to 20% solids, that retentate being discharged into membrane unit 16 by pump 21 where it is further concentrated to 40% before discharge into the product tank 17.

Permeate from the second membrane unit 15 and the third membrane unit 16 contains an average surfactant level of 5 ppm and is continuously fed back to the first membrane unit 14. The process operates continuously with cleaning being carried out once per week using cleaning tank 22 and associated valves and pumps.

Thus, as in the case of the batch process described with reference to Fig. 1, in the continuous process described with reference to Fig. 2 the only outputs are reusable latex delivered to tank 17 and reusable water delivered to tank 18.

With both the batch and continuous processes described above, the energy consumption is a little more than 50% of the total energy consumption of conventional equivalent plant which uses reverse osmosis in association with pre-filtering using ultrafiltration. Furthermore, the capital cost of a reverse osmosis only plant is obviously considerably less than a combined reverse osmosis and ultrafiltration plant. Thus the present invention provides very significant economic advantages as compared with the relevant prior art.

CLAIMS

1. A process for separating latex from waste water, wherein the waste water is delivered directly to a reverse osmosis membrane unit, and pressure is applied across a membrane defined by the membrane unit to drive water through the membrane, the membrane unit defining channels through which the waste water is pumped which channels have flow cross sections sufficient to enable flow rates to be maintained that prevent channel blockage.

2. A process according to claim 1, wherein the waste water is delivered to the membrane unit by a diaphragm pump operating at a speed of at least 1,000 strokes per minute and a pressure of at least 35 barg.

3. A process according to claim 2, wherein a batch of waste water is delivered from a feed source to a batch tank, the waste water is pumped through the membrane channels from the batch tank, the retentate is recirculated to the batch tank, the permeate is delivered to a permeate outlet until the surfactant content of the permeate exceeds a predetermined level, whereafter the permeate is recirculated to the feed source, and the retentate is discharged from the batch tank to a retentate outlet.

4. A process according to claim 3, wherein the pump operates at greater than 1500 strokes per minute and delivers waste water to the membrane unit at a pressure of at least 40 barg.

5. A process according to claim 3 or 4, wherein the said predetermined level is two parts per million surfactant.

6. A process according to claim 2, wherein a continuous feed of waste water is delivered from a feed source to a first reverse osmosis membrane unit, the permeate from the first membrane unit is delivered to a permeate outlet, the retentate from the first membrane unit is delivered to at least one further reverse osmosis membrane unit, the permeate from the at least one further membrane unit is recirculated to the feed source, and the retentate from the at least one further membrane unit is delivered to a retentate outlet.

7. A process according to claim 5, comprising three reverse osmosis membrane units, a second membrane unit receiving retentate

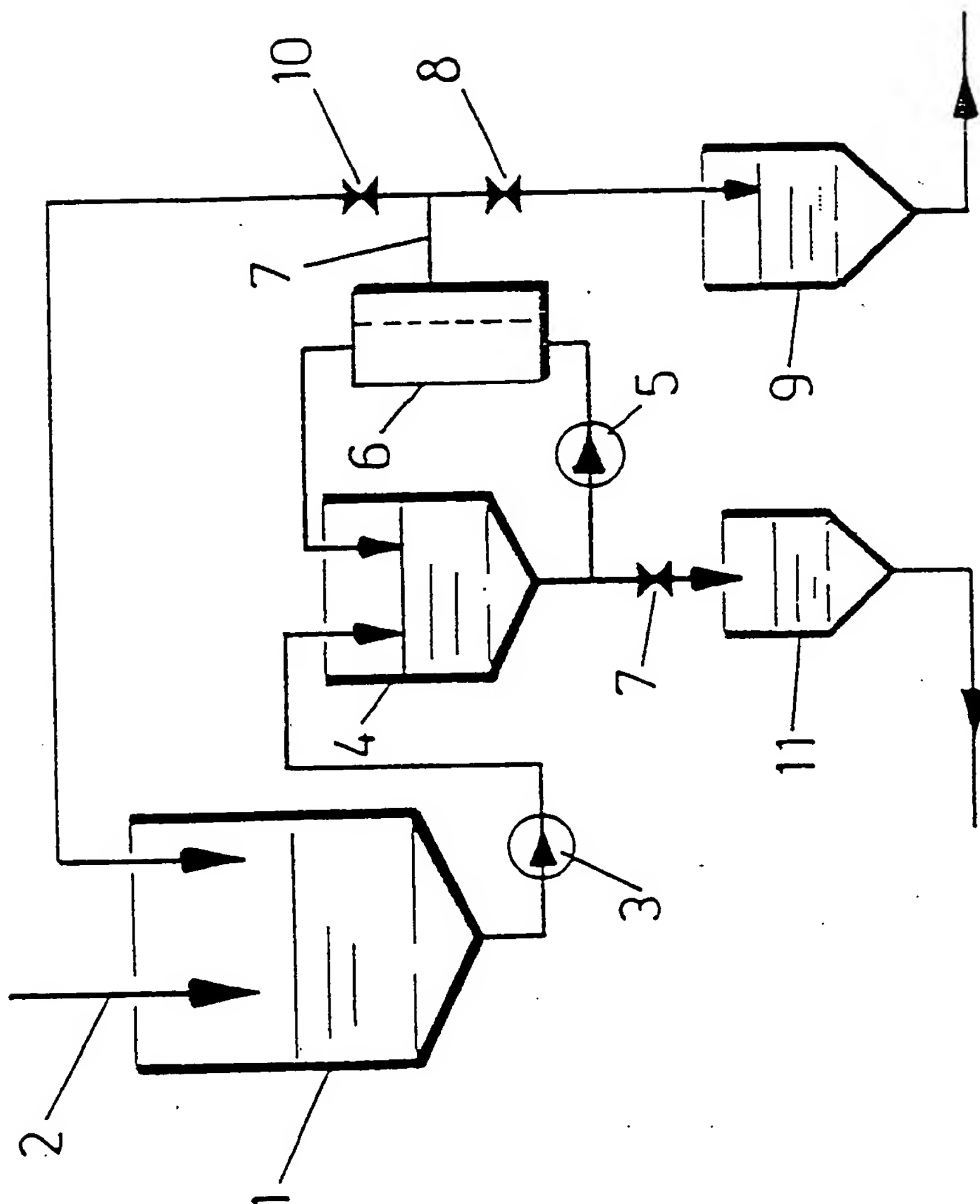
from a first and delivering retentate to a third membrane unit, and the second and third membrane units recirculating permeate to the feed source.

8. A process according to claim 7, wherein waste water is delivered to the first membrane unit by a pump operating at greater than 2,000 strokes per minute and a pressure of at least 35 barg, retentate is delivered to the second membrane unit by a pump operating at greater than 1,500 strokes per minute and a pressure of at least 40 barg, and retentate is delivered to the third membrane unit by a pump operating at greater than 1,000 strokes per minute and at a pressure of at least 45 barg.

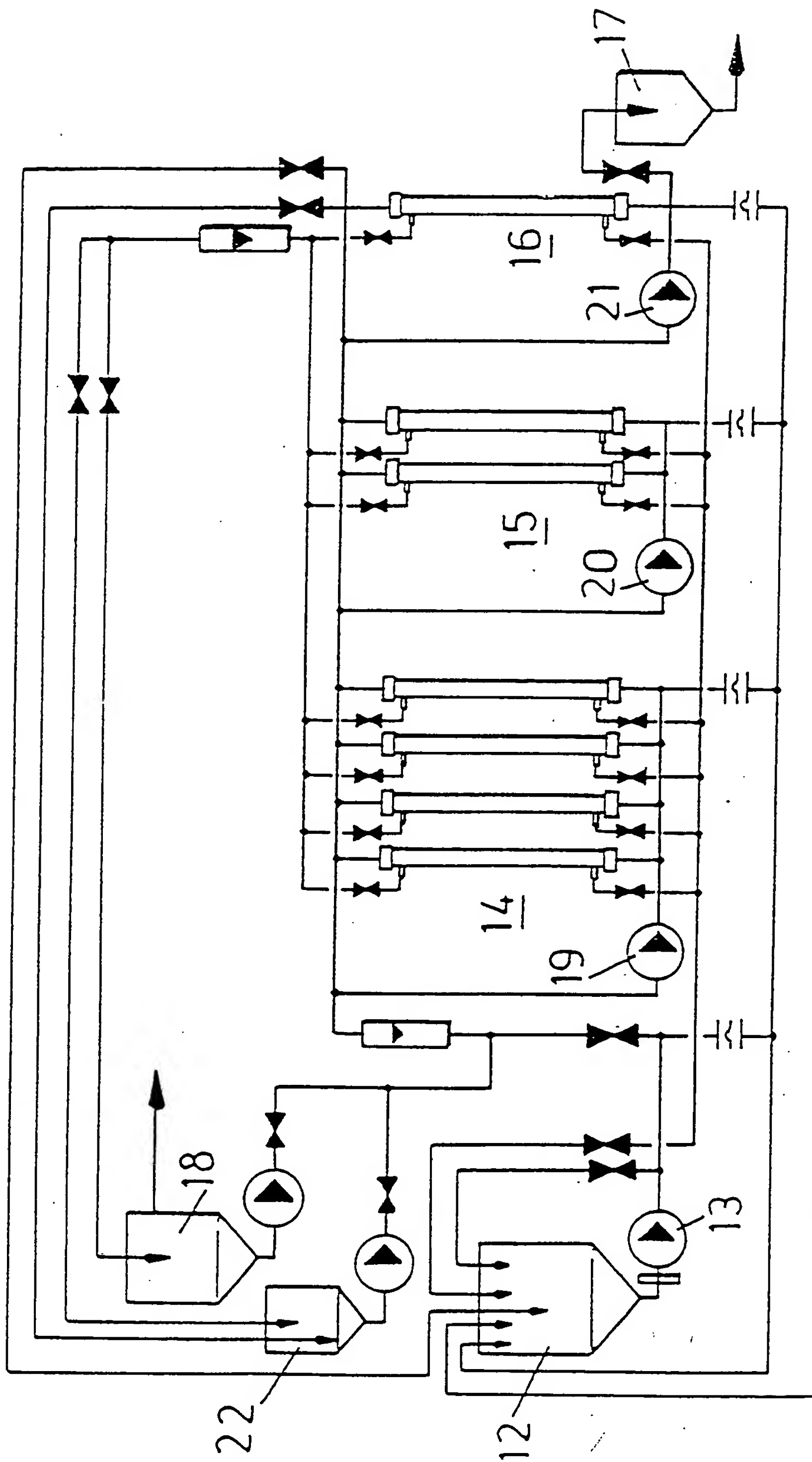
9. A process according to any preceding claim, wherein the or each membrane unit comprises a tubular membrane module.

10. A process according to claim 9, wherein the tubular membrane module defines channels having a diameter of from 10 to 25 mm.

11. A process substantially as hereinbefore described with reference to the accompanying drawings.

FIG. 1

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FIG. 2

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C02F1/44 801D61/02 801D61/10 801D61/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C02F 801D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 527 386 (BAYER AG) 17 February 1993 see abstract; claims 1,2,4,7; examples 1,2 see page 2, line 1 - line 37 see page 3, line 44 - page 4, line 3 see page 4, line 9 - line 10 ---	1,9
A	US,A,4 160 726 (DELPICO) 10 July 1979 cited in the application see abstract; claims 1,3,6,14,15; figure see column 1, line 30 - column 2, line 6 see column 2, line 16 - line 27 see column 2, line 46 - line 58 see column 3, line 12 - line 17 --- -/--	1,9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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